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A facile, sensitive, and highly specific trinitrophenol assay based on target-induced synergetic effects of acid induction and electron transfer towards DNA-templated copper nanoclusters

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ABSTRACT

Reliable, selective and sensitive approaches for trinitrophenol (TNP) detection are highly desirable with respect to national security and environmental protection. Herein, a simple and novel fluorescent strategy for highly sensitive and specific TNP assay has been successfully developed, which is based on the quenching of the fluorescent poly(thymine)-templated copper nanoclusters (DNA-CuNCs), through the synergetic effects of acid induction and electron transfer. Upon the addition of TNP, donor-acceptor complexes between the electron-deficient nitro-groups in TNP and the electron-donating DNA templates are formed, resulting in the close proximity between TNP and CuNCs. Moreover, the acidity of TNP contributes to the pH decrease of the system. These factors combine to dramatically quench the fluorescence of DNA-CuNCs, providing a "signal-off" strategy for TNP sensing. The as-proposed strategy demonstrates high sensitivity for TNP assay, and a detection limit of 0.03 μM is obtained, which is lower than those reported by using organic fluorescent materials. More significantly, this approach shows outstanding selectivity over a number of TNP analogues, such as 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT), 2,4-dinitrophenol (DNP), 3-nitrophenol (NP), nitrobenzene (NB), phenol (BP), and toluene (BT). Compared with previous studies, this method does not need complex DNA sequence design, fluorescent dye labeling, or sophisticated organic reactions, rendering the strategy with additional advantages of simplicity and cost-effectiveness. In addition, the as-proposed strategy has been adopted for the detection of TNP in natural water samples, indicating its great potential to be applied in the fields of public safety and environmental monitoring.

1. Introduction

Nitroaromatic compounds (NACs) are a class of electron deficient compounds, known as explosive materials, and have attracted great attention in recent years due to their military applications, threats of terrorism, and high toxicity to the environment [1]. Thus, rapid, sensitive, and selective detection of NACs is highly desirable. Until now, a variety of methods for NACs detection have been reported, such as mass spectrometry [2], electrochemistry [3], gas chromatography [4], and others. However, most of these techniques are not easily accessible due to the requirements for bulky equipment, relative high cost, time consuming procedure, and complicated manipulations.

Fluorescent chemical sensors, widely used for the detection of various targets and easily applied to fabricate microelectronic devices, are promising optical platforms for simple, sensitive, and selective detection of NACs [5–7]. For fluorescence sensing of NACs, the most frequently used approach is the fluorescence quenching protocol, which is based on the formation of electron-rich fluorescent materials (easily reacted with proton-donating NACs), such as carbon dots [8], organic emitting materials [9], fluorescent polymer compounds [10], and metal-organic architectures [11]. However, the aforementioned electron-rich materials are susceptible to some limitations hampering their application in NACs detection, including the sophisticated organic reaction, weak luminescence, high toxicity, and poor selectivity among NACs [12,13]. To solve such problems, some researchers have reported novel fluorescent sensing materials to achieve simple, sensitive, and selective detection of NACs [14–16]. For instance, Dong's group reported a fluorescent platform for 2,4,6-trinitrotoluene (TNT) analysis based on aqueous carbon dots [14]. Xia et al. developed a strategy by intercalating ruthenium polypyridine complexes into interlayer galleries of layered double hydroxides to fabricate optical molecular material for TNT assay [16]. However, most research on NACs is primarily directed towards the detection of TNT,

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and less attention has been paid to trinitrophenol (TNP), whose explosive power is superior to that of its well-known counterpart TNT [17], and the present TNP sensing protocols cannot distinguish TNP from other NACs, especially TNT. Furthermore, as compared to other NACs, TNP possessed high solubility in water to easily contaminate soil and groundwater, resulting in serious environmental pollution [18]. Therefore, it is highly desirable to develop new sensing materials with simple synthetic processes, excellent luminescence, good stability, and good selectivity for TNP recognition.

Copper nanoclusters have emerged as a novel class of fluorescent probes and among them fluorescent DNA-templated copper nanoclusters (DNA-CuNCs) especially have captured widespread attention [19]. Compared to organic emitting materials and semiconductor dots, DNA-CuNCs are well suitable for the development of fluorescent biosensors due to their outstanding properties, including easy preparation, favorable optical property, high photostability, low toxicity, and long analytical wavelength. DNA-CuNCs have been applied to detect various analytes, such as hydrogen peroxide [20], protein [21], exonuclease III [22], and polynucleotide kinase [23]. However, to the best of our knowledge, there has not been any report on the application of DNA-CuNCs for NACs determination.

Considering the electron deficient ability of TNP and taking advantage of the desirable optical property of DNA-CuNCs, herein, we developed a simple, reliable, and sensitive fluorescent strategy for the specific recognition of TNP in aqueous solutions. In the proposed sensing strategy, poly-T DNA was used as both the template for CuNCs formation and the electron-rich groups reacting with the proton donating target, TNP. Upon the addition of TNP, the resultant DNA-CuNCs-TNP complex shows a significant fluorescence decrease, which is ascribed to the synergetic effects of acid induction and photo electron transfer between TNP and DNA-CuNCs. The fluorescence intensity of DNA-CuNCs in aqueous solution decreases along with the increase of TNP concentration, applied as a readout signal for constructing fluorescent platform for TNP sensing. It was also found that other NACs analogues including TNT, DNT, DNP, NP, NB, BP, and BT showed little contribution to the fluorescence decrease, implying the outstanding selectivity of proposed method for TNP detection. Compared with the previously reported works that commonly involved complex DNA sequence design, fluorescence dye labels, and sophisticated organic reactions, our strategy processes the advantages of high sensitivity, good selectivity, easy preparation, low toxicity, and excellent optical property.

2. Experimental

2.1. Reagents and materials

HPLC-purified poly(thymine), T_{50} with the sequence of 5′-T50–3′, was purchased from Sangon Biotech Company, Ltd. (Shanghai, China). 3-(N-morpholino) propanesulfonic acid (MOPS), copper sulfate, sodium chloride, sodium ascorbate, and other salts were obtained from Dingguo Biotechnology Company, Ltd. (Beijing, China). 2,4,6-trinitrophenol, 2,4,6-trinitrotoluene, 2,4-dinitrotoluene, 2,4-dinitrophenol, 3-nitrophenol, nitrobenzene, phenol, and toluene were purchased from Energy Chemical Company, Ltd. (Shanghai, China). The reagents were of analytical grade and used without further purification or treatment. Ultra-pure water (resistivity >18.2 MΩ cm @25 °C) obtained from a Milli-Q water purification system (Millipore Corp., Bedford, MA, USA) was used throughout the experiments.

2.2. Apparatus

All fluorescence measurements were performed on a Hitachi F-4600 fluorescence spectrometer (Japan) equipped with a xenon lamp as the excitation source and a personal computer as the data processing unit. The slits for excitation and emission were set at 5.0 nm and 10.0 nm, respectively, and the excitation voltage was 700 V. The excitation wavelength was set at 340 nm, and the emission spectra from 520 nm to 660 nm were collected. The fluorescence intensity at 627 nm was used to evaluate the performance of the proposed TNP sensing strategy. UV-Visible absorption spectra were recorded on a UV/Vis/NIR 2600 spectrometer (Shimadzu, Japan) using quartz cuvettes with 1 cm path length. Gel electrophoresis images were obtained on a Bio-Rad Gel Doc XR+system (Hercules, CA, USA). Transmission electron microscopy (TEM) images were recorded on a HT7700 microscope (Hitachi, Japan) operated at 100 kV. The TEM specimens were made by placing a drop of the nanoparticles suspension on a carbon-coated copper grid.

2.3. Synthesis of poly-T-templated CuNCs

DNA-CuNCs were synthesized according to the reported method [19]. In a typical procedure, the stock solutions of Poly T were first diluted to desired concentration in MOPS buffer (10 mM MOPS, 150 mM NaCl, pH 7.4). Then, sodium ascorbate and copper sulfate were added into the poly T solutions, reacting for certain time. The final volume of the solution was brought to 100 μL with MOPS buffer, and the fluorescent signal was measured.

2.4. Fluorescent assay of TNP

The feasibility investigation of TNP sensing was first carried out by detecting TNP dissolved in water. Typically, 90 μL of the synthesized DNA-CuNCs aqueous solution and 10 μL of TNP with different concentrations were incubated for 30 min at room temperature. The fluorescence signals of the mixtures were subsequently recorded.

2.5. Determination of TNP in water samples

The artificial lake water samples were obtained from Qingdao Agriculture University campus. The samples were centrifuged at 12,000 rpm for 20 min twice and then the supernatant was filtered using 0.22 μm water-phase microfiltration membranes. A 50 μL aliquot of the treated water sample spiked with different concentrations of TNP was added into DNA-CuNCs solution. The final volume of the resulting solution was added to 100 μL with MOPS buffer. The fluorescence spectra of the solutions were collected.

3. Results and discussion

3.1. Principle of fluorescence TNP biosensing strategy

Scheme 1 illustrates the general principle of the fluorescence biosensor for TNP detection based on the synergetic quenching effects of acid induction and electron transfer. Upon the addition of Cu^{2+} and ascorbate to poly-T, DNA-templated copper nanoclusters (DNA-CuNCs) were formed, which emitted fluorescence with the maximum emission wavelength of 627 nm. The synthesized DNA-CuNCs also exhibited excellent optical stability, whose fluorescence intensity changed little upon fabrication and stored in air for dozens of minutes. In the presence of TNP, the donor-acceptor complexes between TNP and DNA-CuNCs were formed

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